Evaluating Dimethyldiethoxysilane for use in Polyurethane Crosslinked Silica Aerogels

Jason P. Randall[1], Mary Ann B. Meador[2], and Sadhan C. Jana[1]

[1] University of Akron, Akron, OH, 44325
[2] NASA Glenn Research Center, 21000 Brookpark Rd., Cleveland, OH, 44135

Silica aerogels are highly porous materials which exhibit exceptionally low density and thermal conductivity. Their "pearl necklace" nanostructure, however, is inherently weak; most silica aerogels are brittle and fragile. The strength of aerogels can be improved by employing an additional crosslinking step using isocyanates. In this work, dimethyldiethoxysilane (DMDES) is evaluated for use in the silane backbone of polyurethane crosslinked aerogels. Approximately half of the resulting aerogels exhibited a core/shell morphology of hard crosslinked aerogel surrounding a softer, uncrosslinked center. Solid state NMR and scanning electron microscopy results indicate the DMDES incorporated itself as a conformal coating around the outside of the secondary silica particles, in much the same manner as isocyanate crosslinking. Response surface curves were generated from compression data, indicating levels of reinforcement comparable to that in previous literature, despite the core/shell morphology.

Evaluating Dimethyldiethoxysilane for use in Polyurethane Crosslinked Silica Aerogels

Jason P. Randall[1], Mary Ann B. Meador[2], and Sadhan C. Jana[1]

1. University of Akron, Akron, OH, 44325   2. NASA Glenn Research Center, 21000 Brookpark Rd., Cleveland, OH, 44315

Objective

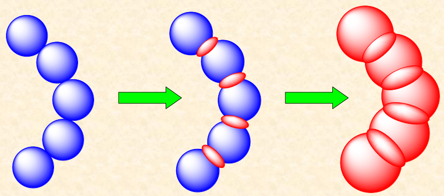
This work seeks to examine the use of dimethyldiethoxysilane (DMDES) in the silane backbone in polyurethane crosslinked aerogels, specifically if it can be used to create more flexible aerogels. The effects of DMDES on the microstructure and physical properties of crosslinked aerogels are eludiated.

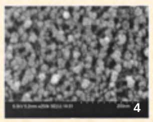
Rationale

- Silica aerogels possess low thermal conductivity and low density, making them highly desirable for thermal insulation applications.

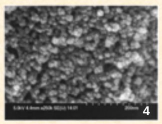
- However, the "pearl necklace" nanostructure of native silica aerogels is inherently weak, requiring only about 31 kPa[4] of stress to completely shatter it.

- This can be improved by employing an additional crosslinking step involving isocyanates, which increases interfacial area between particles without destroying the porosity.





Native Aerogel



Isocyanate Crosslinked Aerogel

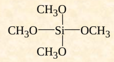
- Crosslinking in this manner has been shown to increase strength by up to a factor of 300, with only about a factor of 2-3 increase in density[4], but tend to yield very brittle aerogels.

- What if the underlying silica framework was partially composed of silanes which form linear chains instead of networks?

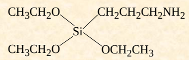
Materials

Silanes

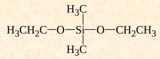
- Tetramethoxysilane (TMOS)



- 3-aminopropyltriethoxysilane (APTES)

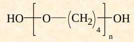


- Dimethyl diethoxy silane (DMDES)

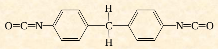


Polyurethane Components

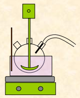
- Polytetramethylene glycol (PTMG)



- Methylenediphenyl diisocyanate (MDI)



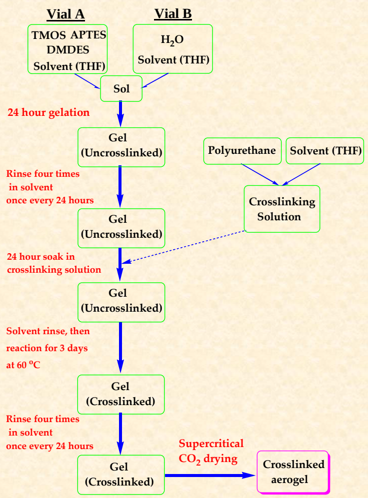
Polyurethane Reaction



1:2.2 molar ratio of PTMG:MDI

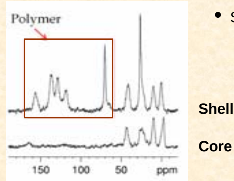
Reaction carried out for 2 hours at 80 °C

Aerogel Reaction



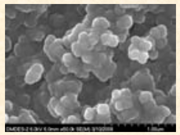
Results and Discussion

- Core-shell morphology was observed in about half the samples, mostly at low DMDES concentration.

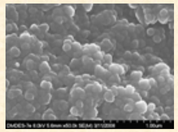


- Solid-state NMR experiments revealed no polymer crosslinking took place in the core of core/shell samples.

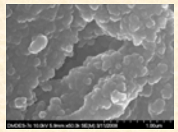
- SEM revealed both uniform and core/shell samples appear coated, similar to isocyanate crosslinking.



Uniform Crosslinked Aerogel



Shell

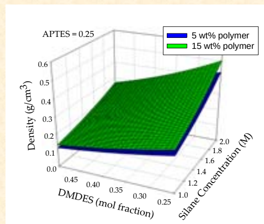


Core

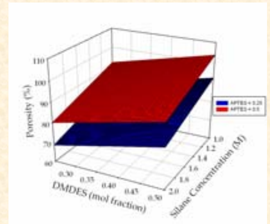
- Since the cores contain no polyurethane, DMDES must incorporate itself as a coating instead of inside the secondary particles.

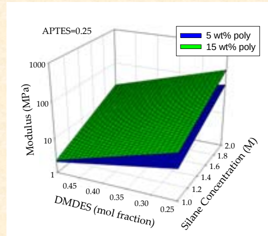
- Density modeling indicated silane concentration is largest factor.

- Increasing DMDES lowered density, likely due to the DMDES coating inhibiting polymer access to APTES.



- Modeling porosity data indicated increasing APTES increased porosity. Given that excess APTES to polyurethane probably existed at low APTES fraction as suggested by the core/shell morphology, increasing APTES further only reduced the number of silane crosslink sites available to 3 per Si from 4 for TMOS.





- Modeling compression data once again showed increasing silane concentration to have the largest effect on increasing modulus.

- Increasing DMDES decreased strength, likely due to the DMDES coating inhibiting polymer uptake.

Conclusions

- DMDES incorporates itself as a coating on the surface of the secondary particles, much like in isocyanate crosslinking.
- Increasing DMDES decreased density and modulus due to the coating inhibited the polyurethane's access to APTES to react.
- DMDES did not flexibilize the aerogels as hoped, due to the location of its incorporation
- Developing control over producing the core/shell morphology could lead to aerogels with maximum strength on the outside, yet maximum thermal resistivity on the inside.

References

1. http://images.usoutdoorstore.com/usoutdoorstore/products/full/vsq_radiator_blkred_07.jpg Accessed July 2008
2. http://stardust.jpl.nasa.gov/photo/aerogel.html
3. www.synlube.com/images/sojourner.jpg
4. Zhang, G., Dass, A., Rawashdeh, A.-M. M., Thomas, J., Counsil, J.A., Sotiriou-Leventis, C., Fabrizio, E.F., Ilhan, F., Vassilaras, P., Scheiman, D., McCorkle, L., Palczer, A., Johnston, J.C., Meador, M.A., Leventis, N. *J. Non-Crystalline Solids*. **2004**, 350, 152

Acknowledgements

The authors would like to thank Linda McCorkle for the SEM micrographs. The authors would also like to thank Bayer Corporation for supplying the MDI, and the NASA Graduate Research Fellowship Program for funding.